# **Chapter 10: Experimental Results**

Electrical energy is input to the polypyrrole/electrolyte system, resulting in mechanical energy output. The primary aim of this chapter is to characterize the electromechanical behavior of polypyrrole films. Linear system identification techniques are employed to measure the polymer electrical admittance (inverse impedance), the strain to charge transfer function, and the stress to charge transfer function. The magnitude of the admittance reveals the rate of charge transfer that can be achieved as a function of frequency, which in turn impacts on the strain rate and power to mass. The phase of the admittance indicates the relative magnitudes of electrical energy dissipation and storage mechanisms as a function of frequency, with implications for electrical to mechanical conversion efficiency. The strain and stress to charge ratios are measures of the electrical to mechanical coupling.

The results are employed to calculate efficiency of electrical to mechanical energy conversion, the strain to charge coefficient,  $\alpha$ , power to mass ratio and other important figures of merit. The "diffusive-elastic-metal" model presented in Chapter 8 is fit to the results, and used to interpret frequency response.

# **10.1 Polypyrrole Sample Properties**

Some basic properties of the films employed in the experiments presented are summarized in Table 1. Uncertainties are largely due to uncertainties in measured film dimensions. The current densities and temperatures at which the films are grown are  $1.1\pm0.2 \text{ A}\cdot\text{m}^{-2}$ ,  $-45\pm4$ °C (8.5 µm film),  $1.7\pm0.2 \text{ A}\cdot\text{m}^{-2}$ ,  $-37\pm3$ °C (12 and 44 µm films) and  $2.0\pm0.3 \text{ A}\cdot\text{m}^{-2}$ ,  $-32\pm3$ °C (51 µm film). Note that film conductivity increases as synthesis temperature is reduced, as has been observed previously (Yamaura, Hagiwara and Iwata 1988). Film age is found to be important, with older films losing the ability to actuate.

Film	Thickness	Conductivity	Modulus	Modulus	Density	Date	Date
	(µm)	$(kS \cdot m^{-1})$	Dry	Wet	Dry	Grown	Measured
			(GPa)	(GPa)	$(kg \cdot m^{-3})$		
1.	8.5±2	43±5	1.4±0.1	0.7±0.2	$1800 \pm 200$	1Mar00	April-
							Jun00
2.	44±2	32±5		0.73±0.04		4Feb00	18Apr00
3.	51±3	22±5	1.8±0.1	0.72±0.04	1500±200	1Dec98	Feb99 &
							Apr00
4.	12±2	35±4		0.8±0.2		2Feb00	18Mar00
<b>Table 1</b> : Basic electrical and mechanical properties of the films tested.							

# **10.2 Polymer Solvent Content**

Soaking of films in electrolyte and pure propylene carbonate results in solvent insertion, and, as will be shown, swelling, a reduction in film stiffness and little change in conductivity. It will also be shown in a later section that admittance increases significantly during swelling. These findings have implications for the mechanisms involved.

Immersion of the 8.5  $\mu$ m thick polymer into 0.3 M (C<sub>2</sub>H<sub>5</sub>)<sub>4</sub>NPF<sub>6</sub> in propylene carbonate (PC) leads to an increase in polymer mass of 25±3%. Soaking the film in pure propylene carbonate leads to a mass change of 21±3%, suggesting that most, if not all, of the mass change observed is due to solvent insertion. Drying the unsoaked film at 90 °C in a nitrogen atmosphere leads to a mass loss of 21.7 %, as shown in Figure 1<sup>\*</sup>. The rate of mass loss, also shown in Figure 1, is consistent with a diffusion limited process. Drying of a pure PC soaked film under vacuum at 90°C leads to a mass loss of 41±3 %. These results suggest that the 40 to 50 % mass difference between dry and wet is due to solvent content. The effect of this flux on mechanical properties is now examined.

<sup>&</sup>lt;sup>\*</sup> The mass loss is measured using a Perkin Elmer TGA7 thermal gravimetric analyzer (<u>www.perkinelmer.com</u>).

Figure 1.

Figure 2.

#### **10.3 Passive Mechanical Properties**

Polypyrrole passive constitutive response (no applied current) and tensile strength are important to their use. The magnitudes of creep/stress relaxation, plastic deformations, and of the ultimate tensile strength will all place limits on the actuator applications. Changes in response between dry and wet states provide some insight into polymer structure.

#### 10.3.1 Dry to Wet Transition

Immersion of polypyrrole films into 0.3 M ( $C_2H_5$ )<sub>4</sub>NPF<sub>6</sub> in propylene carbonate (PC) leads to film stretching and to a decrease in stiffness. Figure 2 shows the extent of stretching of a film held at 3 MPa. The creep observed over a similar time scale in a wet film is less than 2 %. Immersion also leads to a drop in stiffness from 1.4 GPa to 0.7 GPa<sup>\*</sup>, as shown in Figure 3, calculated to produce < 1 % strain, so that the total stretching attributable to soaking is ~12 %. If swelling is isotropic the calculated volume change is ~40 %. The 25% mass change upon swelling suggests a volume change of ~38 %, assuming that PC is causing the mass change, and that its density its maintained upon insertion into the polymer. Thus the observed extent of swelling is consistent with the mass increase due to propylene carbonate insertion.

Over a period of 40 hours after soaking, during which the force on the film is held constant, 20 % extension in length is observed, accompanied by a rise in film end to end resistance from 45.4  $\Omega$  to 50.4  $\Omega$ . The polypyrrole film resistance rises by 15% (after

<sup>&</sup>lt;sup>\*</sup> Changes in film width and thickness as a result of immersion in solvent have not been accounted for in calculating the wet modulus.

accounting for the contact resistance of 11.7  $\Omega$ ). Interestingly, despite polymer mass increase, film conductivity is not greatly affected.

Does the solvent fill pores, the spaces between molecules or both? This question is relevant to the understanding of mass transport of solvent and dopant ions into the polymer. Given that propylene carbonate accounts for 40-50 % of the total mass of the wet polymer, there is roughly one propylene carbonate molecule for every pyrrole unit. If solvent primarily fills pores then the force required to produce a given film displacement is not expected to decrease. However, if the solvent is affecting intermolecular interactions, thereby plasticizing the polymer, a large reduction in stiffness is expected. The observed halving of film stiffness upon soaking strongly suggests that propylene carbonate is affecting intermolecular interactions by penetrating between chains or filaments, and thus at least some of the solvent is reaching inter-chain spaces, and is not simply stored in pores.

If solvent is invading the intermolecular spaces, rather than pores, it might be anticipated that conductivity would decrease, given the close correlation between polymer conductivity and structure (Kohlman and Epstein 1998). Surprisingly, conductivity is virtually unaffected at room temperature. Kohlman and Epstein suggest that polypyrrole has an inhomogeneous structure, with crystalline regions that are roughly 2 nm in diameter, making up roughly 50% of the polymer in  $PF_6^-$  doped material. These ordered regions are thought to be primarily responsible for the metal-like conductivity, and are surrounded by disordered zones lacking chain orientation. It may be that the large influx of propylene carbonate solvates the incoherent regions. This would explain the large influx of solvent, the negligible change in conductivity on swelling, the decrease in

257

stiffness, and the observations that large anions do not penetrate the polymer (Pei and Inganas 1992).

#### **10.3.2 Stress-Strain Curves**

Figure 4 shows the stress strain curves obtained from a 8.5  $\mu$ m thick film at strain rates of  $4.8 \times 10^{-4} \text{ s}^{-1}$ ,  $2.8 \times 10^{-4} \text{ s}^{-1}$  and  $9.8 \times 10^{-5} \text{ s}^{-1}$ . Strain is shown as a function of time in Figure 5. The data shows that on timescales of several hundreds of seconds the stiffness varies by only about 10%, and thus, to first order, can be modeled as a purely elastic material. Some creep is observed, which is not surprising given that the stresses approach the material tensile strength of ~50 MPa.

A linear viscoelastic model consisting of a spring,  $E_1$ , in series with a parallel spring,  $E_2$ , and dashpot *b* has been fit to the data in Figure 5. The good fit suggests that the behavior is dynamically linear over the timescales tested. Further experimentation is required to determine stress-strain relationships at longer times scales.

Do the mechanical properties of polypyrrole show a dependence on the oxidation state<sup>\*</sup>? No significant change in stiffness is observed when the equilibrium potential is stepped between -0.66 V, -0.26 V and 0.14 V vs. Ag/AgClO<sub>4</sub>. In this experiment step changes in oxidation state were made on a 12  $\mu$ m thick film. Stress-strain measurements were obtained 2000 s after the step changes. Film resistance also remained essentially constant, as expected for polypyrrole over this potential range (Feldman, Burgmayer and Murray 1985).

<sup>\*</sup> Variable stiffness is a key characteristic of mammalian skeletal muscle, very useful in picking up and catching objects.

De Rossi and colleagues have reported that polypyrrole stiffness changes by 50 % over a potential range of -1 V to 1 V vs. calomel (Della Santa, Mazzoldi, Tonci and De Rossi 1997), (-1.7 to +0.3 vs. Ag/AgClO<sub>4</sub>). The larger potential range involves large changes in conductivity and oxidation state (Feldman, Burgmayer and Murray 1985), the latter being associated with increased polymer hydrophobicity (Doblhofer and Rajeshwar 1998). Changes in hydrophobicity may drive out solvent, leading in turn to increased stiffness.

# **10.4 Admittance**

The aim of this section is to find the current to voltage relationship, which provides insight into mechanisms of electrical energy storage and loss, as well as being linked with strain, strain rate, power to mass and efficiency. Linear system identification techniques have been chosen to analyze the polymer/electrolyte cell admittance. The first task is to demonstrate that scaling applies, a necessary characteristic of a linear dynamic system. Next, it is shown that the measured admittances result from current into the polymer films, and are not due to the clamping methods, or parasitic impedances. It is also shown that during the initial immersion of films into solution, the admittance is time-dependent, suggesting that large increases in mass transport rate within polypyrrole result from solvent insertion. Finally, it is shown that mass transport is significantly lower in old films. The slow mass transport in older films allows their double layer capacitance to be estimated. The estimated double layer capacitance is consistent with the predictions of the diffusive-elastic-metal model, which relates volumetric and surface capacitances. The diffusive-elastic-metal model proposed in Chapter 8 is fit to the measured admittances to obtain estimates of diffusion coefficient in several films.

#### **10.4.1** Linearity

Figure 6 shows the measured admittance at 0.1 V and 0.5 V peak swept sine amplitudes. Scaling is obeyed over nine decades in frequency. The linear behavior over a range of 1 V suggests that the electron transfer kinetics and Nernstian reactions are not playing a significant role in the response over the frequency range probed. At sufficiently high amplitudes and low frequencies the polymer degrades, with black streaks of material

being ejected from the polymer surface. These become obvious at applied potential amplitudes of greater than 2 V over time scales of more than 20 s in 8.5  $\mu$ m thick films. Further experimentation is needed to characterize the degradation, and determine its effect on actuation and cycle life.

#### 10.4.2 Surface/End Currents

Does a significant portion of the current flow through the clamped ends, bypassing the portion of the polymer film exposed to the solution? Are there parasitic admittances through which a significant portion of the current flows, or which modify the expected applied voltage (e.g. voltage drop across the reference electrode)? Also, how much of the admittance is due to interactions at the polymer surface as opposed to within polypyrrole? The contributions of surface and end effects are estimated by comparing polymer admittance with the admittance obtained using a stainless steel electrode of similar width and length.

After measuring polypyrrole admittance, the film is cut and removed from solution, such that only the clamped sections remain. Next, a 'dummy' stainless steel electrode, having the same width and length as the original polymer film, is inserted in the clamps and electrically connected, with the ends of polymer remaining. The admittance of the dummy configuration is then taken, and the two admittances are compared.

At high frequencies, where the solution resistance is expected to dominate response, the two admittances should be very similar. However, diffusion is expected to dominate polymer response at intermediate frequencies, producing much higher admittances than obtained from the dummy electrode.

Figure 7 compares the admittance of an 8.5 µm thick, 50 mm long, and 2.1 mm wide polypyrrole film held between clamps 30 mm apart, with admittances from a stainless steel electrode of the same width and length, and having the 10 mm clamped sections of the polymer film still present. As expected the admittance is nearly identical at high frequencies. At intermediate frequencies the dummy electrode has a much lower admittance, suggesting that surface and end effects represent a small part of the total polymer current in this range. Below 10 mHz the dummy electrode current is significant relative to the polymer current. The phase of the polymer admittance begins to drop in the same frequency regime, contradicting model predictions that it remain purely capacitive. Thus surface and end effects appear to influence polymer admittance at low frequency. However, over most of the range tested, the clamping method and surface interactions (other than double layer capacitance at high frequency) play a negligible part in determining the measured polymer admittance.

#### **10.4.3 Admittance During Swelling**

Polypyrrole films clearly absorb propylene carbonate. How does this uptake affect admittance? Figure 8 compares the admittance taken soon after soaking in electrolyte with that taken 13 hours later. The response is identical at high and low frequencies, but clearly admittance increases at intermediate frequencies. An admittance time sequence taken during the swelling described in sections 10.2 and Figure 2 is shown in Figure 9. Note that the change in admittance essentially ceases after about 9000 s, which corresponds to the time at which the rate of length change, Figure 2, drops dramatically. The simultaneous changes in polymer mass, length and admittance strongly suggest that

increases in admittance are due to increased current within the polymer. Is the internal current limited by mass transport, kinetics, or thermodynamics?

Kinetics limited behavior is expected to be independent of frequency and to increase exponentially with applied potential – clearly not the case here. If the thermodynamics dominate, the state of charge must be a function of the potential alone, and the current will therefore increase in direct proportion to frequency. Such behavior is observed at low frequencies, where the response appears capacitive, but not at intermediate frequencies. Therefore, mass transport into the polymer is the rate-limiting factor at intermediate frequencies and the inclusion of solvent is facilitating mass transport.

#### 10.4.4 Estimating Double Layer Capacitance: Swelling and Aging

The high electronic conductivity of polypyrrole, and the expected low rate of dopant mass transport compared with that in the liquid electrolyte, suggest that double layer charging of the polymer electrolyte interface will occur. The diffusive-elastic-metal model (presented in Chapter 8) predicts that the double layer capacitance, C, and volumetric capacitance,  $C_V$ , are related:

$$C_{V} = C \cdot \left(\frac{a \cdot C}{2 \cdot k \cdot \varepsilon_{0} \cdot A} + 1\right).$$

$$1$$

Confirmation of the model would be obtained if this relationship can be shown to hold.

The admittance data does not show an RC charging curve that allows double layer capacitance to be clearly identified. This is likely due to high rates of mass transport into the polymer, which act to discharge the double layer. Two effects enable estimates of double layer capacitance to be made. Immediately after immersion in electrolyte, rates of

mass transport are relatively small, presenting an opportunity to measure double layer capacitance. Secondly, it is found that in older films, mass transport into the bulk is negligible, allowing the extent to surface charging to be measured.

Figures 9 and 10 show an attempt to fit a first order model to the unswollen polymer. The first order model, represented by the dashed lines, represents a capacitance of  $0.6 \text{ F} \cdot \text{m}^{-2}$ . However, as is particularly evident from the linear plot in Figure 10, it is not obvious how to fit, or even if the fit is valid. This is not terribly surprising, since the outer polymer volume likely becomes infused with solvent more rapidly than the measurements can be made. Only the slight rise in phase near 3 kHz provides a clue that diffusion has become dominant.

The admittance of a  $51\pm3$  µm thick film grown on the 1<sup>st</sup> of December 1998, and stored in an airtight polyethylene bag for 1 year and four months, is shown in Figure 11. The rapid drop in admittance below 100 Hz, as opposed to 10 mHz in the other films shown so far, suggests that mass transport into the polymer is limited. Also plotted in Figure 11 is the admittance of a stainless steel dummy electrode, scaled in amplitude and shifted in frequency to fit the polymer film admittance. The two data sets match very closely, suggesting that the observed polymer admittance is indeed primarily due to surface effects. Finally, no perceptible strain or stress is observed in response to applied voltage, again indicating surface rather than bulk activity. The same form of response is found in two other films of similar age.

271

On the strength of these findings, a first order series *R*, *C* model is fit to the admittance data, as depicted by the red line in Figure 11. Note that the frequency responses of both the stainless steel electrode and of the polypyrrole do not have the expected slope of 1 decade/decade in the log/log plot at low frequencies. This may be due to surface reactions, or end charging effects. Whatever the reason, these additional effects will serve to increase the admittance. The resistance is fit to the high frequency data, and the capacitance is chosen such that model magnitude is always less than or equal to the measured value and the model phase equals or exceeds the measured phase. The resulting fit suggests that the double layer capacitance is  $0.3 \text{ F}\cdot\text{m}^{-2}$ . Step current measurements show that a 2 month old film taken from the same sample has volumetric capacitance of  $7\pm1\times10^7 \text{ F}\cdot\text{m}^{-3}$ , which corresponds via Equation 1 to a predicted double layer capacitance of  $0.28\pm0.06 \text{ F}\cdot\text{m}^{-2}$ . The diffusive-elastic-metal model prediction is reasonable.

What is the polymer aging process and how are properties other than admittance affected? This question is important in helping determine the limits on actuator shelf life. The film conductivity is  $2.2\pm0.5\times10^4$  S·m<sup>-1</sup> after 1 year and 4 months in storage, essentially unchanged from that measured 2 months after synthesis of  $2.4\pm0.5\times10^4$  S·m<sup>-1</sup>. The density is also found to be unchanged, at  $1.5\times10^3$  kg·m<sup>-3</sup>, as is the stiffness in the dry state, at 1.8 GPa. However, while the young film expands by more than 7.5 % upon immersion in electrolyte, the older film shrinks by 1%. No charge induced strain is observable in the aged film, while the two month old film actuated readily with a strain to charge ratio of  $1.3\times10^{-10}$  C·m<sup>-3</sup>.

Aging affects the ability to absorb solvent, limiting mass transport, but leaves conductivity, density and dry elastic modulus unaffected. More work needs to be done to identify the cause of the drop in permeability, and to determine whether or not it is reversible or preventable. If it cannot be reversed, or prevented, by, for example storage in solvent, then there is clearly a major limitation on polymer actuator shelf life. It is encouraging that conductivity does not decrease, suggesting that no major changes in the polymer chemistry have occurred.

#### **10.4.5** Comparison of Modeled and Measured Admittances

The next stage is to fit the model presented in Chapter 8 to the data, and compare responses. Two approaches are taken. In the first, measured values of volumetric capacitance and resistance are used. The diffusion coefficient, D, is then found which best fits the data. In the second approach, in cases where the solution resistance has not been measured, resistance, R and diffusion coefficient, D, are adjustable, and used to find the best fit. It is demonstrated that the diffusive-elastic-metal model is able to fit the admittance data within experimental uncertainty, providing an excellent parametric description over most of the frequency range tested.

#### 10.4.5.1 Will a simpler model work?

The model in Chapter 8 is a function of film surface area, film thickness and three additional variables (diffusion coefficient, D, double layer capacitance, C, and resistance, R). Before fitting it, is interesting to investigate a description with only two additional variables – namely resistance,  $R_2$ , and capacitance,  $C_2$ , in series. At first glance, a high pass filter seems to exhibit the same frequency response, namely high frequency

admittance that is constant and real, and low frequency admittance that is capacitive. Simplicity is this model's advantage.

Figure 12 is a comparison of the first order model response and admittance data from an 8.5 µm thick film. The resistance used in the model is the sum of the measured electrolyte resistance, the metal-polymer contact resistance and the calculated probe to polymer resistance. (The latter is used to account for the finite size of the probe used in measuring the solution resistance.) The measured solution resistance is  $28\pm3 \Omega$ , and the contact resistance is 3.0±0.5  $\Omega$ , yielding a total cell resistance  $R=31\pm4 \Omega$ . The effective volumetric capacitance obtained from step current measurements is  $7\pm2\times10^7$  F·m<sup>-3</sup>, as presented in Chapter 7, with the error term accounting for differences between films and uncertainties in the measurement of film dimensions. The resulting first order model is shown in red, with error bars representing the uncertainties in measured R and C. The model predicts the response within experimental uncertainty at high and low frequencies, but provides a poor description between 10 mHz and 10 Hz. For some applications and on some time scales the first order model may be sufficient. It represents a limiting case of Equation 17 in Chapter 8, in which  $R \cdot C >> a^2 \cdot (4 \cdot D)^{-1}$  - the double layer charges much more slowly than diffusion time constant.

#### **10.4.5.2** Fitting the Diffusion Coefficient

The next step is to fit the full model of admittance, *Y*:

$$Y(s) \cdot R = s \cdot \frac{\frac{\sqrt{D}}{\delta} \cdot \tanh(\frac{a}{2} \cdot \sqrt{\frac{s}{D}}) + \sqrt{s}}{\frac{\sqrt{s}}{R \cdot C} + s^{3/2} + \frac{\sqrt{D}}{\delta} \cdot s \cdot \tanh(\frac{a}{2} \cdot \sqrt{\frac{s}{D}})}, \qquad 2$$

where *R* is the reference to working electrode resistance, including the resistance of contacts and leads, *D* is the polypyrrole ionic diffusion coefficient, *a*, is the film thickness, *C*, is the double layer capacitance, *s* is the Laplace variable and  $\delta$  is the estimated double or Debye layer thickness, expressed in terms of dielectric constant, *k*, surface area, *A* and permittivity of free space,  $\varepsilon_0$ :

$$\delta = \frac{k \cdot \varepsilon_o \cdot A}{C}.$$

At low frequency,  $|s| \ll a^2 \cdot D^{-1}$ , and  $|s| \ll R \cdot C$  the admittance is purely capacitive:

$$Y(s) = s \cdot C \cdot \left(\frac{a}{2 \cdot \delta} + 1\right) = s \cdot C_V.$$

All the variables are measured directly, except the double layer capacitance, *C* and the diffusion coefficient, *D*. The double layer capacitance is calculated using Equation 1 and the volumetric capacitance,  $C_V$ , measured in Chapter 5 ( $C_V=1.3\pm0.2\times10^8$  F·m<sup>-3</sup>). The diffusion coefficient is left as a free parameter. The range of diffusion coefficients is found which allows the model and measurements to fit within experimental uncertainty.

Figure 13 shows the results of fitting the model (central red line) to the data (blue dots). The enveloping red lines represent extrema of model prediction based uncertainties in the measured parameters. The following measured values are employed:

- Film thickness,  $a=8.5\pm2 \mu m$ ;
- Double layer capacitance,  $C=28\pm5 \mu$ F;
- Resistance,  $R=31\pm4 \Omega$ .

The diffusion coefficient is  $2.1\pm0.7\times10^{-12}$  m<sup>2</sup>·s<sup>-1</sup>. Differences between the model fit and the data are less than 14 %. The model form and measured response are somewhat different at the frequency extremes. Below 1 mHz the phase drops. This is likely due to surface and end effects, as discussed in section 10.4.2. Above 10 kHz there is a slight rise in phase, which is corrected by accounting for the non-ideal response of the potentiostat (Chapter 9), as can be seen in Figure 14. There is also a gradual rise in admittance above 100 Hz that is not accounted for by the model or the potentiostat corrections. The rise is also seen in measurements made of the counter electrode to film admittance<sup>\*</sup>, and the measured stainless steel electrode admittance, both shown in Figure 14. The differences may be the result of non-uniform charging of the polymer/electrolyte interface at high frequencies, with the film edges charging before the remainder of the polymer surface.

<sup>&</sup>lt;sup>\*</sup> The counter to polymer admittance measurement is made using an HP4194A impedance analyzer. The low frequency portion of the response, where counter electrode impedance is significant, is not shown.

#### **10.4.6 Effect of Ion Concentration**

A number of models predict a diffusion-like response, but are based on transport through electrolyte filled pores rather than diffusion between polymer chains. The most popular is the porous metal model, in which capacitance is due to double layer charging of electrolyte filled pores within a highly conductive solid, and mass transport within the pores is driven by electric fields (Bull, Fan and Bard 1982; Mao, Ochmanska, Paulse and Pickup 1989; Amemiya, Hashimoto and Fujishima 1993; Posey and Morozumi 1966). Diffusion-like behavior is the result of a combination of charge migration into pores and double layer charging of the pore walls, forming a transmission line. Could the apparent diffusion observed be the result of charging pores? A simple means of distinguishing between pore charging and other forms of 'diffusion' is to change electrolyte concentration. Lowering concentration lowers pore conductivity, increasing the diffusion time constant. Diffusion rates that are independent of electrolyte concentration indicate that pore charging is not significant.

The admittance measurements described in the previous section are repeated using 0.05 M instead of 0.3 M tetraethylammonium hexafluorophosphate in propylene carbonate. The resulting admittance is shown in Figure 15. Also shown are two model curves. The red curve assumes that the diffusion coefficient is unchanged from the 0.3 M case, whereas the black curve uses a diffusion coefficient that is reduced by the ratio of electrolyte conductivities. The relatively good correspondence obtained using the same diffusion coefficient, and the poor agreement using the reduced diffusion coefficient are strong indications that pore charging does not explain the observed admittance.

#### **10.4.7 Effect of Film Thickness**

The diffusive elastic metal model predicts that the time scale of the transition from a diffusion limited regime to a volumetric capacitive regime,  $\tau_D$ , is a function of film thickness, a, and of the diffusion coefficient, D, namely  $\tau_D = a^2 \cdot (4 \cdot D)^{-1}$ . As an initial check on the validity, the model is fit to the admittance of a 44 µm thick film. Figure 16 shows the results of fitting the model (red lines) to the data (blue dots). The red lines represent the mean and the extrema of model prediction based uncertainties in the measured parameters. The following measured values are employed:

- Film thickness,  $a=44\pm3 \mu m$ ;
- Double layer capacitance,  $C=28\pm5 \mu$ F;
- Resistance,  $R=41\pm4 \Omega$ .

The diffusion coefficient is estimated to be  $6\pm 2\times 10^{-13}$  m<sup>2</sup>·s<sup>-1</sup>, where the range indicates values that enable the modeled and measured gains and phases to agree within experimental uncertainty. The bottom plot is the magnitude of the difference between predicted and measured admittances relative to the measured values.

The fit is poor in the top and bottom decades in frequency. The systematic offset in the top decade is a result of the 100 pF input capacitance of the HP3562A dynamic signal analyzer, combined with the 100 pF capacitance of the coaxial cable attached to the reference electrode, and the 69 k $\Omega$  impedance of the Ag/AgClO<sub>4</sub> reference. These effects are added to the model shown in Figure 17, providing a very convincing match to the observed admittance.

The poor fit below 1 mHz is likely due to sources of current not accounted for by the model, including surface electrochemical reactions, losses to mechanical work, and current flow into the clamped polymer ends. The admittance was measured with the film cut, leaving only the clamped ends. The resulting admittance is subtracted from the original observed admittance and plotted in Figure 16 (green dots), resulting in an improved match in gain and phase between 0.1 and 1 mHz. Thus end effects may play a large role in the drop in phase and the flattening in gain at low frequency.

The corrected curve fits very well over the entire frequency range. The diffusion coefficient is a factor of 3 smaller than is estimated for the 8.5  $\mu$ m thick film.

Figure 18 shows the measured and modeled admittances from a 53 µm thick film in 0.05 M tetraethylammonium hexafluorophosphate. The measured admittance transfer functions are obtained by taking the fast Fourier transform of the current observed in response to a 0.2 V step about an equilibrium potential of -0.19 V vs. Ag/AgClO<sub>4</sub>, sampled at 10 Hz, the and at 100 Hz. The solution resistance is not measured, so both the diffusion coefficient and the resistance are fit, and found to be  $D=7\pm2\times10^{-12}$  m<sup>2</sup>·s<sup>-1</sup> and  $R=180\pm30$   $\Omega$ . The uncertainties are chosen such that the model forms an envelope about the 10 Hz data. The form of the response over 4 orders of magnitude again provides strong evidence behavior governed by the diffusion equation. The rise in phase below 10 mHz is an indication that the diffusion time constant has been reached. The estimated diffusion coefficient is once again significantly different from those estimated in the other films.

The model provides a good description of the admittance in 8.5  $\mu$ m and 44  $\mu$ m thick films with one adjustable parameter, and for the 51  $\mu$ m thick film with two adjustable parameters. The next question is, do the parameters reflect the underlying physical mechanisms?

#### **10.4.8** Discussion of Admittance Model

The general form of the model matches the admittance response within experimental error over nine orders of magnitude in frequency. The most significant deviations from the model behavior occur below 1 mHz and above 1 kHz. The former appear to be due to end effects and possibly surface reactions, and the latter are likely due to variations in resistance as a function of position along the film. These can be resolved by making measurements in better-defined geometries, in which the current density at the film surface is uniform. This may require that measurements be made with the polymer attached to a conductive substrate.

If it is accepted that the mathematical form of the model is correct, the question still remains as to whether the assumptions on which the model is built are correct. Diffusion coefficient and double layer capacitance need to be measured independently. Diffusion coefficient may be measured using NMR techniques, for example. If the measured dopant diffusion coefficient matches that estimated by the model, it provides a strong affirmation. If the diffusion coefficient is similar to that of dopants in propylene carbonate, then migration, diffusion and convection through pores may play a role.

Direct measurement of polymer double layer capacitance is difficult because mass transport across the double layer appears to simultaneously discharge this capacitance while charging is underway. In order to observe double layer charging directly, the model predicts that the *R*·*C* time constant must be smaller than the double layer diffusion discharge time constant,  $\delta^2 \cdot D^{-1}$ , where  $\delta$ , is the double layer thickness. The most obvious approach to obtaining small *R*·*C* charging times is to reduce the reference electrode to polymer surface distance. Given the solution conductivity of 0.5 S·m<sup>-1</sup> and typical double layer capacitances in the range of 0.1-0.4 F·m<sup>-2</sup>, diffusion coefficients on the order of 10<sup>-12</sup> m<sup>2</sup>·s<sup>-1</sup>, and double layer thicknesses of 1 nm (estimated using equation 3), the reference to polymer distance will have to be less than 1  $\mu$ m<sup>\*</sup> in order to overcome the effects diffusion discharge, and allow double layer charging to be directly observed.

The estimated diffusion coefficients are quite different from film to film, ranging from  $0.6 \times 10^{-12} \text{ m}^2 \cdot \text{s}^{-1}$  to  $7 \times 10^{-12} \text{ m}^2 \cdot \text{s}^{-1}$ . If the model is to be believed, then these differences may be the result of differences in synthesis conditions, extent of exposure to water, the length of immersion in solution, or some other variables. It will be important to determine which factors influence the apparent diffusion coefficient, because strain rate is proportional to current, and current is in turn limited by diffusion.

 $<sup>^*</sup>$  The reference could be a thin wire rather than a standard electrode such as calomel, Ag/AgCl or Ag/AgClO<sub>4</sub>.

# 10.5 Relationship between Strain and Charge

Is the strain proportional to the amount of charge per unit volume transferred to or from polypyrrole, as has been suggested in Chapter 5, and how is the strain to charge ratio affected by the applied voltage and load? In order to investigate the effect of charge on strain, films are held under isotonic conditions and swept sine potentials are applied between polymer films and reference electrodes. The transfer function between strain and current is recorded, from which the strain to charge ratio is determined.

The diffusive-elastic-metal model presented in Chapter 8 predicts that strain,  $\varepsilon$ , in response to an electrical stimulus applied to a polymer of volume,  $V_f$ , is proportional to charge transferred, Q:

$$\varepsilon = \frac{\alpha \cdot Q}{V_f}, \qquad 5$$

where  $\alpha$  is the empirical constant of proportionality known as the strain to charge ratio. Transforming Equation 5 into the Laplace domain, and re-expressing it in terms of current, yields:

$$\frac{\varepsilon}{I} = \frac{\alpha}{s \cdot V_f}.$$
 6

Equation 6 defines the strain to current transfer function, which may also be expressed in terms of current per unit volume:

$$\frac{\varepsilon}{\dot{\rho}} = \frac{\alpha}{s} \,. \tag{7}$$

#### **10.5.1** Linearity of the Strain to Charge Ratio

Figure 19 shows that the strain to current transfer function in an 8.5 µm thick film held at 1 MPa follows has the form of Equation 6. Furthermore, the response is unaffected by the magnitude of applied potential, suggesting that the system is dynamically linear. The measured range of linear response is -0.7 to +0.3 V vs. Ag/AgClO<sub>4</sub> at frequencies between 200 µHz and 1 Hz and -1.2 to +0.8 V vs. Ag/AgClO<sub>4</sub> between 8 mHz and 2 Hz. At frequencies below 8 mHz, degradation in response is noticeable when  $\pm 1$  V is applied. The strain to charge ratio,  $\alpha$ , of  $1.2\pm0.3\times10^{-10}$  m<sup>3</sup>·C<sup>-1</sup> agrees within experimental error with those estimated using step response methods, presented in Chapter 5. The total strain at 1 V (2 V peak to peak) is 1.8 %, and represents a change in oxidation state of roughly 1 charge for every 8 monomers.

#### **10.5.2 Strain to Charge and Film Thickness**

Figure 20 shows the measured strain to current transfer function from of 8.5  $\mu$ m, 12.5  $\mu$ m and 44  $\mu$ m thick films, and all held under between 1 MPa and 4 MPa force per cross-sectional area. The strain to charge ratios are in the range of 1.0±0.4 m<sup>3</sup>·C<sup>-1</sup>. Strain to charge ratio is independent of film thickness. The strain to charge ratios are nearly independent of frequency, except in the case of the 12.5  $\mu$ m film, held at 4 MPa, which appear to undergo a transition in strain to charge ratio between 10 mHz and 100 mHz.

#### 10.5.3 Load Dependence of the Strain to Charge Ratio

Figure 21 shows the strain to charge ratio as a function of applied stress in a 12.5  $\mu$ m thick film. The strain to current transfer function is taken at 4 MPa, 30 MPa and 40 MPa. The strain to charge ratio is  $1.5 \times 10^{-10} \text{ m}^3 \cdot \text{C}^{-1}$  for all loads at frequencies above 100 mHz. However, it drops between 10 and 100 mHz, with the extent of the shift increasing with load, such that at 40 MPa the strain to charge ratio is  $0.4 \times 10^{-10} \text{ m}^3 \cdot \text{C}^{-1}$  below 10 mHz. The phase also undergoes a transition between 10 and 100 mHz. The phase shift away from the predicted –90° difference between strain and current suggests that dissipation is occurring. The stress strain curves in Figures 4 and 5 indicate that the creep is significant over the same time scale. The mechanisms of visco-elastic relaxation may be the same as those responsible for the reduction in strain to charge ratio.

#### **10.5.4** Strain to Charge Summary

Strain rate is proportional to current. The constant of proportionality is nearly independent of frequency at stress levels of 4 MPa or less, over a frequency range of 0.1 mHz to 1 Hz, and for applied potentials up to 0.5 V peak, and 1.0 V peak. The constant of proportionality is found to be  $1.0\pm0.4$  m<sup>3</sup>·C<sup>-1</sup>, matching the strain to charge ratios measured in Chapter 5. The use of higher applied voltages to increase strain rate and power to mass is discussed in Chapter 11. Large loads (>10 MPa) are associated with substantial creep (several percent), which may be responsible for the observed decrease in strain to charge ratio as frequency is decreased (Figure 21), and definitely impacts on actuator performance.

Does the strain to charge ratio remain constant at higher frequencies? Measurement of the strain to current transfer function is limited by the closed loop response time of the apparatus. The stress to current transfer function enables the response at higher frequencies to be probed.

### **10.6 Relationship between Stress and Charge**

Given that strain is proportional to charge then, under isometric conditions, it is anticipated that stress,  $\sigma$ , will also be a function of charge transferred, and that the stress to charge,  $\beta$ , and strain to charge,  $\alpha$ , ratios are be proportional to each other via the relationship:

$$\frac{\sigma}{\dot{\rho}} = \frac{\beta}{s} = \frac{E \cdot \alpha}{s} \,. \tag{8}$$

This is shown to be the case in Chapter 5. As confirmation, swept sine voltage inputs are applied to films held isometrically, and the stress to current transfer function is measured. Figure 22 plots the stress to charge observed in same film from which the strain to charge in Figure 21 is obtained. As expected, strain is proportional to charge, and division by the measured elastic modulus of 0.8 GPa, yields a strain to charge ratio estimate of  $1.5\pm0.4 \text{ m}^3 \cdot \text{C}^4$ , compared with  $1.5\pm0.3 \text{ m}^3 \cdot \text{C}^4$  estimated from the strain to current transfer function above 0.1 Hz in Figure 22. Note that, as with the strain to charge, the phase of the stress to charge ratio rises below 0.1 Hz, again suggesting a relaxation effect within the polymer.

Figure 23 is a plot of the stress to current ratio from an 8.5  $\mu$ m thick film. As expected, strain is proportional to charge, and division by the measured elastic modulus of 0.7 GPa, yields a strain to charge ratio estimate of 1.5±0.4 m<sup>3</sup>·C<sup>-1</sup>, compared with 1.2±0.2 m<sup>3</sup>·C<sup>-1</sup> estimated from the strain to current transfer function of the same film, Figure 20.

The measurements shown in Figure 23 are the result of 1000 averages. Force output from the strain gauge amplifier is passed through a 1 kHz low pass filter. The variance

accounted for drops sharply near 60 Hz. Power spectrum measurements confirm that the major source of noise in the force measurement is due to 60 Hz coupling.

The fact that stress changes are observed at frequencies in excess of 30 Hz is consistent with observations of bilayer actuators presented in Chapter 7 (Madden, Cush, Kanigan and Hunter 2000). The equivalent strain rate is estimated to be  $0.4 \% \cdot s^{-1}$ .

# **10.7 Efficiency**

The electrical to mechanical conversion efficiency is the ratio of output work to input electrical energy. The efficiency is calculated by using the admittance measurements to obtain the electrical energy input as a function of frequency and the strain to current measurements to provide work done. At low frequencies a large portion of the input electrical energy is stored, and can be recovered. Efficiency is therefore calculated in two ways, one assuming that stored energy is recovered, and the second that it is not. When energy is recovered, the relationship between efficiency, *e*, admittance phase,  $\angle Y$ , magnitude of applied voltage, *V*, applied stress,  $\sigma$ , and strain to charge ratio,  $\alpha$ , is given by Equation 28 in Chapter 8:

$$e = \frac{2 \cdot \sigma \cdot \alpha(\omega)}{\pi \cdot / V / \cdot \cos(\angle Y(i\omega))}.$$
9

In calculating efficiency, the strain to charge coefficient,  $\alpha$ , is determined from the measured strain to current transfer function. If energy is not recovered, Equation 29 in Chapter 8 gives the efficiency:

$$e = \frac{2 \cdot \sigma \cdot \alpha}{|V| \cdot \gamma(\angle Y(i\omega))},$$
10

where

$$\gamma = \frac{\pi}{180} \cdot \cos(\angle Y) \cdot (180 - \angle Y) + \sin(\angle Y).$$
 11

These calculations are performed using the data measured from a 12.5  $\mu$ m thick film held at 4 MPa and 30 MPa, and activated with swept sine inputs having an amplitude of 0.1 V peak about  $V_{eq}$ =-0.2 V vs. Ag/AgClO<sub>4</sub>, as depicted by the red and blue points and crosses in Figure 24. Data obtained using large loads is deliberately chosen to maximize measured efficiency, and thereby explore the limits of polypyrrole performance. The measured strain to current transfer function obtained from this film is shown in Figure 21. The magnitudes of the error bars are primarily determined by uncertainties in measurement of phase.

Model predictions are also shown for both cases, as represented by the lines. The predicted efficiency, with energy recovery is (Chapter 8, Equation 42):

$$e = \frac{2 \cdot \sigma \cdot \alpha}{/V / \cdot \pi \cdot \cos(\angle Y) + 2 \cdot \sigma \cdot \alpha},$$
12

and without is (Chapter 8, Equation 43):

$$e = \frac{2 \cdot \sigma \cdot \alpha}{/V / \cdot \gamma + 2 \cdot \sigma \cdot \alpha}.$$
 13

In equations 12 and 13 the modeled admittance (Equation 2 this Chapter) is used in place of the measured admittance. The strain to charge ratio,  $\alpha$ , is assumed to be independent of frequency, with a value of  $1.5 \times 10^{-10}$  m<sup>3</sup>·C<sup>-1</sup>, obtained by fitting to the measured strain to charge ratio in Figure 21 over a frequency range of 0.1 to 1 Hz.

With no energy recovery, the efficiency at 4 MPa is  $0.6\pm0.2$  %, and is relatively independent of frequency, while at 30 MPa efficiency reaches  $3\pm1$  %. Note that the model (dashed lines) predicts a rise in efficiency with decreasing frequency due to the reduction in electrical energy expenditure as the current increases in phase relative to the

applied voltage. However, the measured efficiency drops between 10 mHz and 100 mHz reflecting the drop in strain to charge ratio, as seen in Figure 21. The model does not account for the frequency and load dependence of the strain to charge ratio. This frequency dependence is not observed with smaller applied loads (~ 1MPa, Figure 19), leading to good agreement between experiment and model in such cases. While the measurements in Figure 24 do not follow the model, they do show the highest efficiencies obtained using swept sine measurements. The large loads overcome the reduction in efficiency due to the drop in strain to charge ratio.

How does the efficiency depend on applied voltage? In previous sections it is shown that actuator response to voltage inputs is linear over a range of at least  $\pm 0.5$  V, and that at moderate loads (~1 MPa) the strain to charge ratio is independent of frequency and voltage. Because strain is proportional to charge, increasing the applied voltage will proportionally increase mechanical work at constant load. However, the electrical energy increases as the square of the applied voltage, so for constant load, efficiency is inversely proportional to applied voltage. Equivalently, efficiency is greatest at small strains. The voltage dependence of efficiency is eliminated if the actuator works against an untensioned spring rather than a constant load. However, the efficiencies obtainable are lower because limits on the achievable strain prevent large load levels from being achieved.

The measured mechanical energy produced by the polymer is less than  $1/30^{\text{th}}$  the electrical energy input, and drops to less than  $1/100^{\text{th}}$  at low frequency. Clearly, if the strain to charge ratio can be increased, and a larger proportion of the input energy can be recovered, then the efficiency is improved. Improving strain to charge involves changes

in material synthesis and processing. Energy dissipation is proportional to the cosine of the phase. The closer the phase angle is to  $\pm 90^{\circ}$ , the greater the energy storage. Figures 6 through 18 present admittances from various polypyrrole films. The maximum energy recovery is typically achieved at 1 mHz frequencies, with phase  $\leq 85^{\circ}$ , implying an energy recovery of  $\leq 91$  %. What prevents more energy from being recovered?

The polymer acts as a very large capacitor at low frequencies, but some dissipation remains. There are several possible sources of energy loss, including mechanical work, surface reactions with the electrolyte, electrical resistance of the polymer and contacts, end effects and bulk polymer reactions. The end and surface effects are significant at low frequency, their magnitudes suggesting that they are the predominant factors limiting electrical energy storage efficiency, as discussed earlier in this chapter. In Figure 16, the end effects have been subtracted (green points) from the measured polymer admittance, leading to an increase in phase between 0.1 mHz and 1 mHz. Thus, over the frequency range investigated, improvements in efficiency may simply be a matter of changing clamping and film geometries to reduce surface and end effects, providing that effective means of energy recovery can be found.

If polypyrrole actuators in their current forms are to compete with other technologies on the basis of efficiency, electrical energy recovery is necessary, as is operation at frequencies that are lower than the diffusion time constant. In order to obtain high speed, power to mass and efficiency simultaneously, thin, highly conductive films in low resistance electrolytes are required.

## **10.8 Overview**

The admittance, strain to charge and stress to charge transfer functions of polypyrrole films immersed in tetraethylammonium hexafluorophosphate, propylene carbonate electrolyte have been measured. The responses appear linear over a range of +0.3 to - 0.96 V vs. Ag/AgClO<sub>4</sub> at frequencies between  $10^{-4}$  Hz and  $10^{5}$  Hz. A model that describes admittance using a double layer capacitance in parallel with a diffusion element, and in series with solution resistance, fits the data within experimental error, and suggests that diffusion coefficients of dopants within the polymer are in the range of 0.4 to  $7 \times 10^{-12}$  m<sup>2</sup>·s<sup>-1</sup>.

The measured response is not greatly affected by changes in electrolyte salt concentration, demonstrating that migration in electrolyte filled pores is not responsible for mass transport into the polymer. The correlation between increased solvent content, polymer swelling, and greatly increased admittance indicate that the presence propylene carbonate assists mass transport within polypyrrole. The reduction in stiffness observed upon swelling suggests that inter-chain interactions are being affected, and thus that at least part of the propylene carbonate content fills intermolecular spaces and not large pores. Absence of swelling, of increase in admittance, and of active strain in films over one year old demonstrate that permeability is reduced over time, and that shelf life may become an issue that will limit applications.

The strain to charge ratio is  $1.1\pm0.4\times10^{-10}$  m<sup>3</sup>·C<sup>-1</sup>, independent of film thickness, frequency and applied stress at loads of ~1 MPa or less. The stress to charge ratio is equal to the strain to charge ratio,  $\alpha$ , multiplied by the elastic modulus, so that for loads

of ~1 MPa or less, strain,  $\varepsilon$ , is related to stress,  $\sigma$ , charge per unit volume,  $\rho$ , and elastic modulus, *E*, by:

$$\varepsilon = \frac{\sigma}{E} + \alpha \cdot \rho \,. \tag{14}$$

When loads of 30 MPa and 40 MPa are applied, the strain to charge shows a large frequency dependence, shifting from  $1.5 \times 10^{-10}$  m<sup>3</sup>·C<sup>-1</sup> above 100 mHz to  $< 0.5 \times 10^{-10}$  m<sup>3</sup>·C<sup>-1</sup> at low frequencies. Stress-strain curves show a transition from elastic to visco-elastic response over similar time scales, suggesting that the mechanisms are related.

The efficiency with which electrical energy is converted to mechanical energy is dependent on load, amplitude of the applied voltage, frequency and whether or not stored electrical energy is recovered. The highest measured efficiency is 3 %, reaching  $7\pm2$  % if stored electrical energy were recovered. Efficiency increases with decreasing applied potential and therefore is highest at small strains.

# **10.9 Reference List**

- Amemiya, T., Hashimoto, K. and Fujishima, A. Frequency-Resolved Faradaic Processes in Polypyrrole Films Observed by Electromodulation Techniques: Electrochemical Impedance and Color Impedance Spectroscopies. Journal of Physical Chemistry, 1993, 97, 4187-4191.
- Bull, Randy A., Fan, Fu-Ren F. and Bard, Allen J. Polymer Films on Electrodes. Journal of the Electrochemical Society, 1982, 129(5), 1009-1015.
- Della Santa, A., Mazzoldi, A., Tonci, C. and De Rossi, D. Passive Mechanical Properties of Polypyrrole Films: a Continuum Poroelastic Model. Materials Science and Engineering C, 1997, 5, 101-109.
- Doblhofer, Karl and Rajeshwar, Krishnan. Electrochemistry of Conducting Polymers. Skotheim, Terje A.; Elsenbaumer, Ronald L., and Reynolds, John R., Editors.

Handbook of Conducting Polymers. 2nd ed. New York: Marcel Dekker; 1998; pp. 531-588.

- Feldman, B. J., Burgmayer, Paul and Murray, Royce W. The Potential Dependence of Electrical Conductivity and Chemical Charge Storage of Poly(Pyrrole) Films on Electrodes. Journal of the American Chemical Society, 1985, 107, 872-878.
- Kohlman, R. S. and Epstein, Arthur J. Insulator-metal Transistion and Inhomogeneous Metallic State in Conducting Polymers. Skotheim, Terje A.; Elsenbaumer, Ronald L., and Reynolds, John R., Editors. Handbook of Conducting Polymers. 2nd ed. New York: Marcel Dekker; 1998; pp. 85-122.
- Madden, John D., Cush, Ryan A., Kanigan, Tanya S. and Hunter, Ian W. Fast Contracting Polypyrrole Actuators. Synthetic Metals, 2000 May, (113), 185-193.
- Mao, Huanyu, Ochmanska, Jolanta, Paulse, Chris D. and Pickup, Peter G. Ion Transport in Pyrrole-Based Polymer Films. Faraday Discussions of the Chemical Society, 1989, 88, 165-176.
- Pei, Qibing and Inganas, Olle. Electrochemical Application of the Bending Beam Method. 1. Mass Transport and Volume Changes in Polypyrrole During Redox. Journal of Physical Chemistry, 1992, 96(25), 10507-10514.
- Posey, F. A. and Morozumi, T. Theory of Potentiostatic and Galvanostatic Charging of the Double Layer in Porous Electrodes. 1966; 113, (2): 176-184.
- Yamaura, M., Hagiwara, T. and Iwata, K. Ehancement of Electrical Conductivity of Polypyrrole Film by Stretching: Counter Ion Effect. Synthetic Metals, 1988, 26, 209-224.